

# REPORT DOCUMENTATION PAGE

Form Approved  
OASD No. 0704-0188

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1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE January 31, 1996 3. REPORT TYPE AND DATES COVERED Final, April 1, 1991 - Nov. 30, 1995

## 4. TITLE AND SUBTITLE

Study of the Compression Behavior of High Performance Fibers

## 5. FUNDING NUMBERS

62102F  
2419/00

## 6. AUTHOR(S)

Satish Kumar et al.

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Georgia Tech Research Corporation  
Office of Contract Administration.  
Atlanta GA 30332-0420

AFOSR-TR-96

0130

## 8. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NC  
Building 410, Bolling AFB DC  
20332-6448

## 10. SPONSORING / MONITORING AGENCY REPORT NUMBER

AFOSR-91-0194

## 11. SUPPLEMENTARY NOTES

## 12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release distribution unlimited

## 12b. DISTRIBUTION CODE

19960320 054

## 13. ABSTRACT (Maximum 200 words)

Compression behavior of pitch and PAN based carbon fibers and its dependence on structure and morphology has been studied. Structure development in PAN based fibers with heat treatment temperature has been followed using raman spectroscopy. Compressive strength of glassy resins has been studied. Crosslinking in the free annealed methyl pendant PBZT fibers have been verified using <sup>13</sup>C solid state NMR. Based on the axial compressive strength, torsional modulus, and transverse compressive strength measurements, it is concluded that crosslinking remains a viable approach for improving compressive strength in polymeric fibers. Torsional modulus as a function of temperature has been measured for various high performance fibers. Poly(benzobisthiazole)s containing an ortho-tetra substituted biphenyl moiety were synthesized via the polymerization of 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2,2'-dinitro-6,6'-dimethylbiphenyl-4,4'-dicarboxylic acid. PBO and PBZT solubilization mechanism in nitromethane using aluminum chloride has been investigated using solution <sup>27</sup>Al NMR.

## 14. SUBJECT TERMS

## 15. NUMBER OF PAGES

## 16. PRICE CODE

## 17. SECURITY CLASSIFICATION OF REPORT

## 18. SECURITY CLASSIFICATION OF THIS PAGE

## 19. SECURITY CLASSIFICATION OF ABSTRACT

## 20. LIMITATION OF ABSTRACT

14 MAR 1996

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## Annual (Interim) Technical Report

### 1. EXECUTIVE SUMMARY

Title: Study of the Compression Behavior of High Performance Fibers

Principal Investigator: Satish Kumar, Associate Professor

Co -investigator: Malcolm B. Polk, Professor

Inclusive Dates: April 1, 1991 - November 30, 1995

Grant number: AFOSR-91-0194

#### 1.1 Research Personnel:

1. Dr. N. Venkatasubramanian - post-doctoral fellow
2. Dr. Hao Jiang - post doctoral fellow
3. Dr. Victor Kozey - post-doctoral fellow
4. Vinay Mehta - Ph.D student (Graduated winter 1996)
5. C. P. Chang - M.S. student (Graduated spring 1994)
6. Xiaodong Hu - Ph.D. student (expected graduation date Fall 1996)

List of publications and theses produced/in progress as a result of full/partial support from this project are listed below. Since these publications and theses are readily available in the literature, therefore copies of these documents are not enclosed with this report, as per the AFOSR guidelines for the final reports. Summary and conclusions are given after the List of publications and theses.

#### 1.2 Publications:

1. N. Venkatasubramanian, M.B. Polk, Satish Kumar, and L.T.Gelbaum;

- "Structural Investigations on Lewis Acid-Mediated Solubilization of poly (p-phenylenebenzobisthiazole) in an Aprotic Solvent". J. Polym. Sci. (Phys ed.), 31 (1993) p. 1965-1973.
2. Satish Kumar, D.P.Anderson, and A. S. Crasto, "Carbon Fiber Compressive Strength and its Dependence on Structure and Morphology", J. Mater. Sci, 28 (1993) 423-439.
  3. V. V. Kozey and S. Kumar, "Compression Behavior of Materials: Part I - Glassy Polymers", J. Mater. Res., vol. 9, (1994) p. 2717-2726.
  4. V. R. Mehta and Satish Kumar, Temperature Dependent Torsional Properties of High Performance Fibers and their Relevance to Compressive Strength " J. Mater. Sci., vol 29, (1994) p. 3658-3664.
  5. M. Sahafeyan and Satish Kumar, "Tensile and Compressive Behavior of Poly(para-phenylene benzobisthiazole) fibers, J. Appl. Polym. Sci., vol 56 (1995) p. 517-526.
  6. V. V. Kozey, H. Jiang, V. R. Mehta, and S. Kumar, " Compressive Behavior of Materials - part 2: High Performance Fibers", J. Mater. Research, vol. 9 (1995) p. 1044-1061.
  7. V. R. Mehta, S. Kumar, M. B. Polk, D. L. Vanderhart, F. E. Arnold, and T. D. Dang, "On the evidence of crosslinking in the methyl pendent PBZT fiber". Accepted for publication in J. Polym. Sci., Polym. Phys.
  8. X. Hu, S. Kumar, and M. B. Polk, "Synthesis and Characterization of Poly(benzobisthiazole) with a Substituted Biphenyl Moiety in the Main

Chain". Accepted for publication in Macromolecules.

9. J. W. Connolly, D. S. Dudis, S. Kumar, L. T. Gelbaum, and N. Venkatasubramanian, On the Structure of the Soluble Lewis Acid PBZT and PBO complexes. Accepted for publication in Chemistry of Materials.

### 1.3 Theses:

1. C. P. Chang, "Raman Spectroscopic Studies on Carbon Fibers", M. S. Thesis, Georgia Institute of Technology, Atlanta GA, June 1994.
2. V. R. Mehta, "Compression Behavior of High Performance Polymeric Fibers and its Dependence on Crosslinking", Ph. D. Thesis, Georgia Institute of Technology, Atlanta GA, March 1996.
3. X. Hu, "Synthesis and Characterization of Poly(benzobisazole)s with Substituted Biphenyl Moieties in the Main Chain", Ph. D. Thesis, Georgia Institute of Technology, Atlanta GA, in progress.

## 2. TECHNICAL SUMMARY

### 2.1 REVIEW OF COMPRESSION BEHAVIOR OF HIGH PERFORMANCE FIBERS:

Axial compression behavior of high-performance polymeric and carbon fibers has been reviewed. Seven test methods used for determining the compressive strength of single fibers have been compared. Various micro-mechanical models proposed in the literature to understand the compressive failure in single filaments

and in other anisotropic systems have been discussed and analyzed. The results of various approaches to influence the compressive strength of polymeric fibers have been summarized. Possible reasons for the variation in the compressive strength of pitch and PAN based carbon fibers have also been addressed . (V. V. Kozey, H. Jiang, V. R. Mehta, and S. Kumar, " Compressive Behavior of Materials - part 2: High Performance Fibers", J. Mater. Research, vol. 9 (1995) p. 1044-1061.)

## 2.2 TENSILE AND COMPRESSIVE TESTING OF RIGID-ROD POLYMERIC FIBERS:

Heat treated PBZT fiber tested in tension resulted in two types of failure modes. In failure mode I, the fiber exhibits a relatively sharp break; mode II is characterized by significant axial fiber splitting. Approximately 20% of the fibers failed in mode II, when tested at 2.54, 7.62, and 12.7 cm gage lengths. At 1.25 cm gage length all the fibers failed in mode I. Tensile strength decreased from 1.25 to 7.62 cm gage length, but tensile strength of the fibers tested at 7.62 and 12.7 cm gage lengths were similar. The two failure mode observation is supported by the Weibull statistical distribution. Fiber tensile properties were also measured at 150°C. Fiber retains 80% of its room temperature tensile strength and modulus at 150°C. Axial compressive strength of the PBZT fibers as determined from the recoil test is also reported and is found to be independent of fiber tensile modulus and fiber diameter. As received heat treated fibers were post heat treated between 700 and 775°C. Structural changes in the fiber were studied using infra red spectroscopy, small and wide angle x-ray scattering, and swelling studies. Fiber post heat treatment between

725 and 775°C for 30 seconds resulted in reduced fiber swelling and enhanced crystallite size and higher order along the chain axis. No evidence of crosslinking was observed in these post heat treated fibers. (M. Sahafeyan and Satish Kumar, "Tensile and Compressive Behavior of Poly(para-phenylene benzobisthiazole) fibers, J. Appl. Polym. Sci., vol 56 (1995) p. 517-526.)

### 2.3 TORSIONAL MODULUS and its relationship with COMPRESSIVE STRENGTH:

A simple arrangement for the measurement of torsional moduli of high performance fibers as a function of temperature has been reported. Torsional modulus and damping factors have been measured on a number of polymeric [Kevlar™, PBO, PBZT, and Vectran™] and carbon fibers [pitch and PAN based], as a function of temperature [room temperature to 150°C] and as a function of vacuum level [1.1 to  $80 \times 10^3$  Pa]. At these vacuum levels damping in these fine fibers is mainly due to aerodynamic effects. In general PAN based carbon fibers have higher torsional moduli than pitch based carbon fibers. Kevlar 149, PBO, and PBZT have comparable room temperature torsional moduli. Torsional modulus of vectran fiber is very low, and is likely a result of the flexibility of the -COO- group. In the above temperature range the torsional modulus of both pitch and PAN based carbon fibers do not change significantly. For polymeric fibers, torsional modulus decreases with increase in temperature; a small decrease is observed for PBO and PBZT, and a significantly higher decrease is observed for Vectran™. Relationship between torsional moduli and compressive strength have been discussed. ( V. R. Mehta and

S. Kumar, Temperature Dependent Torsional Properties of High Performance Fibers and their Relevance to Compressive Strength " J. Mater. Sci., vol 29, (1994) p. 3658-3664. )

## 2.4 CARBON FIBERS

The axial compressive strength of carbon fibers varies with the precursor material and with the axial tensile modulus. While the development of tensile modulus and strength has been the subject of numerous investigations, increasing attention is now being paid to the fiber and the composite compressive strength. Pitch and PAN based carbon fibers with wide ranging moduli and compressive strength were chosen for a study of compressive strength and its dependence on structure and morphology. Based on this study, the following conclusions were reached: (i) For carbon fibers from a given precursor, compressive strength decreases with increase in tensile modulus. However, by influencing the structure and morphology, the compressive strength can be increased for a given modulus. This is true for both Pitch and PAN based fibers. (ii) For a given modulus, the compressive strength of PAN based carbon fibers is higher than the compressive strength of either pitch based or rayon based carbon fibers. (iii) The crystallite size  $L_c$  ranges from 1.5 nm in low modulus PAN based fibers to 25 nm in high modulus pitch based fibers. The corresponding values for  $L_a(0)$  and  $L_a(90)$  range from 2 to 64 nm and 4 to 88 nm, respectively. The (002) d-spacings for these fibers range 0.3376 to 0.344 nm. This range is somewhat narrower than previously reported, where



corrections for Lorentz and structure factors were not applied. The azimuthal FWHM for the (002) reflection reported as  $Z$  is in the range of 5 to 37°. (iv) High resolution scanning electron microscopy indicates sheet like morphology in all pitch based fibers, even in low modulus P25, where no three dimensional order is observed from WAXS. With an increase in fiber modulus, the sheet boundaries become more defined. In most PAN based fibers, a particulate rather than sheet like morphology was observed. The particulate was observed even in high modulus PAN based M60J carbon fiber, in which three dimensional order is observed from WAXS. These results indicate that sheet like morphology does not necessarily imply a three dimensional order (e.g. P-25). On the other hand, a fiber with particulate morphology can display three dimensional order (e.g. M60J). The PAN based GY70 shows well developed graphite sheets and three dimensional order. (v) Considering the various structural parameters and morphology of the fiber, the variations in crystallite size  $L_c$  and  $L_a(0)$ , the crystallite anisotropy  $L_c L_a(0)/L_a(90)$ , and the development of sheet like structure in the fiber seem to be the factors responsible for the significant compressive strength differences in various fibers. Other crystallite dimensions also have some influence. (vi) The fiber compressive strength can be improved for a given modulus, if the desired (002) orientation in the fiber can be achieved with smaller crystallite size. Controlling the development of sheet like character is also likely to help. (Satish Kumar, D.P.Anderson, and A. S. Crasto, "Carbon Fiber Compressive Strength and its Dependence on Structure and Morphology", J. Mater. Sci, 28 (1993) 423-439.)

Raman spectroscopic studies have been carried out on experimental PAN carbon fibers heat treated at different temperatures (fiber stabilized at 270°C, stabilized fiber heat treated at 400°C, 800°C, 1700°C and at 2800°C). For comparison, raman studies have also been carried out on selected pitch and PAN based commercial fibers. In the early stages (800°C) of carbonization of PAN, a very broad raman band centered around 1317  $\text{cm}^{-1}$ , with width from 1600 to 1000  $\text{cm}^{-1}$  is observed. Such a broad single band has not been reported previously in carbon materials. However the fact that a distinct band at 1575  $\text{cm}^{-1}$  is not observed, also suggests that the graphitic structure has not yet begun to form. The broad band centered at 1317  $\text{cm}^{-1}$  corresponds to the D line, which is attributed to significant disorder or to the development of diamond like structure. At higher heat treatment temperatures this band split into two narrow bands, commonly referred to as D and G bands. Compressive strength has been related to the relative integrated intensities of the D and the G lines. Compressive strength decreased as the relative integrated intensities ( $A_G/A_D$ ) increased. (C. P. Chang, "Raman Spectroscopic Studies on Carbon Fibers", M. S. Thesis, Georgia Institute of Technology, Atlanta GA, June 1994.)

## 2.5 POLYMERIC RESINS

The compressive behavior of DGEBA epoxy resin cured with different curing agents- aliphatic amine, aromatic amine and polyamide has been investigated. All

tested resins exhibit plastic yielding in compression. The dependencies of compressive yield strength on density, glass transition temperature, pores, test speed, sub- $T_g$  aging have been examined. Compressive yield strength has been found to increase with density and glass transition temperature. The links between the form of stress-strain diagram and shear banding have been investigated. Available failure theories for yielding in glassy polymers have been discussed. The conclusions reached from this study are: (i) Both thermoset and thermoplastic glassy polymers exhibit yielding under compression. On yielding, localization of plastic deformation in the form of shear bands can occur if the stress-strain diagram showed stress softening. (ii) Compressive yield strength of thermoplastic and thermosetting glassy polymers is proportional to their glass transition temperature and density. (iii) Compressive yield strength of glassy polymers does not exhibit a unique dependence on the tensile and shear modulus. Experimental data indicates that the compressive and tensile moduli of glassy polymers are equal. (iv) Compressive yield strength of thermosetting resins does not exhibit a unique dependence on tensile strength. (v) Inclusion of rigid particles, short, or long fibers increases compressive yield strength of glassy polymers. (V. V. Kozey and S. Kumar, "Compression Behavior of Materials: Part I - Glassy Polymers", J. Mater. Res., vol. 9, (1994) p. 2717-2726. )

## 2.6 CROSSLINKING IN METHYL PENDANT PBZT SYSTEM:

A brief discussion and conclusions of the Ph. D. thesis on this topic (V. R. Mehta, "Compression Behavior of High Performance Polymeric Fibers and its Dependence on Crosslinking", Ph. D. Thesis, Georgia Institute of Technology, Atlanta GA, March 1996. ) are listed below:

#### 2.6.1 Discussion:

The relatively poor compressive strength of high performance polymeric fibers such as Kevlar™, PBO and PBZT limits their applications in structural composites. We have examined crosslinking as a possible means of influencing and understanding the compression behavior of rigid rod polymeric fibers. Methyl pendent PBZT was chosen to study the effect of heat treatment induced crosslinking on compressive as well as other mechanical properties. It has been shown using  $^{13}\text{C}$  solid-state NMR that below  $450^{\circ}\text{C}$ , there is no evidence of chemical change or crosslinking. However, swelling studies revealed that heat treatment without tension, even at  $400^{\circ}\text{C}$  renders this fiber insoluble. PBZT fiber tension heat treated for 30 to 60 seconds at  $550^{\circ}\text{C}$  (HT PBZT), required longer time and elevated temperature for dissolution in chlorosulfonic acid (CSA), as compared to the readily formed solution of as-spun PBZT in CSA at room temperature. The intrinsic viscosities of both the AS and the HT PBZT fibers were the same. This suggests no increase in molecular weight and no crosslinking on tension heat treatment of PBZT. From these observations, we conclude that lack of dissolution is only the necessary but not the sufficient condition for crosslinking.

Since crosslinking did not occur below 450°C and the significant main chain degradation of MePBZT begins above 550°C (based on TG-MS data), further heat treatments were carried out in the 450 to 550°C range, in the free and varying tension states in the presence of air and nitrogen. At 450°C, free annealing for 10 minutes resulted in reduction of the methyl intensity and simultaneous growth of a methylene resonance near 38 ppm in the  $^{13}\text{C}$  solid state NMR. While these changes were weak at 450°C (less than 3 %), heat treatment at 550°C resulted in dramatic changes; only about 3 % of the methyl groups remained and a definitive methylene peak was observed at 38 ppm. In the latter sample, the maximum extent of crosslinking was estimated to be about 36 % via methylene linkages between the main chain units. The thermogravimetric analysis indicated that when the MePBZT is held at 550°C in nitrogen, the weight loss increased with time. Qualitatively, combining this observation with the, TG - Mass spectra and with the  $^{13}\text{C}$  solid state NMR, we can say that the mass loss is primarily due to the crosslinking reaction, which results in the evolution of methane.

Crosslinking in the free annealed samples resulted in the skin deep transverse cracks on the fiber surface. On the other hand, PBZT free annealed at 530°C, neither showed chemical changes in the  $^{13}\text{C}$  NMR which could be interpreted as intermolecular crosslinking, nor have these fibers developed the type of transverse cracks, as were seen in the free annealed MePBZT fiber. However, the tension annealed PBZT, occasionally showed different type of surface cracks. The MePBZT fibers free annealed above 475°C developed skin-core structure. Fibers heat

treated in the 475 - 550°C range in nitrogen for 10 minutes under the free condition, did not fibrillate, even after extended treatment in the concentrated chlorosulfonic acid. This suggests some degree of interfibrillar crosslinking in the free annealed MePBZT. In order to prevent the formation of the transverse cracks in the MePBZT, heat treatment was carried out at various tension levels at 530°C. These tension heat treated MePBZT fibers did not exhibit transverse cracks, but, resulted in skin-core structure where the core is fibrillar.

Free annealed MePBZT fibers were either partially or completely insoluble in CSA or MSA, depending on the heat treatment temperature. On the other hand, the skin of the tension annealed samples was completely soluble, while the core was partially insoluble. On the basis of results from  $^{13}\text{C}$  solid-state NMR, morphological examination and swelling studies, it was concluded that the crosslinking takes place above 450°C under free annealing. Under tension, no crosslinking is observed in the skin, as it was completely soluble. Crosslinking in the core of the tension annealed samples is limited to the intrafibrillar regions. The absence of crosslinking in the skin of the tension annealed samples and the surface cracks in the free annealed samples have been explained on the basis of orientational differences between the fiber skin and the core. Based on the selected area electron diffraction (SAED) and dark field imaging studies reported in the literature on the fibers spun from the lyotropic liquid crystalline solutions (viz. PBO, PPTA, etc.), it is reasonable to assume that in the MePBZT fiber also the molecular orientation in the skin is higher than that in the core. Free annealing at high temperature provides sufficient

molecular mobility, which facilitates crosslinking (above 450°C) by permitting necessary axial shifts of the molecules bringing pendent methyl groups (or the radicals) in the neighboring chains together. Such axial shifts may be responsible for the transverse cracks which are generated in the more oriented skin. On the other hand, in the case of tension annealed samples, the chains may not be able to shift and align (as required for the crosslinking) due to the restricted mobility under the applied external constraint. Since the core has lower orientation than the skin, some intra-fibrillar crosslinking may have occurred in the core of the tension heat treated samples.

As expected, the transverse crystallite size and the molecular orientation increased upon free as well as tension heat treatments, with a higher increase being observed on tension heat treatment. Two new equatorial reflections, hitherto not reported, were observed in the case of free annealed PBZT and in free as well as tension annealed MePBZT. This is likely a result of development of a new crystal phase coexisting with and dominated by the monoclinic crystal cell reported in the literature for PBZT (ref).

It is of interest to know, whether the crosslinking in the MePBZT fibers occurred in the crystalline or in the disordered regions. Judging from the free energy confirmations of the various possible crosslinked structures, it appears that the crosslinking in the MePBZT fibers occurs in the disordered regions. This is consistent with the observation of smaller transverse crystallite size in the free annealed MePBZT as compared to the tension annealed MePBZT. We also point out

here that the free annealed PBZT, where no evidence of crosslinking has been reported, shows higher crystallite size as compared to the tension annealed samples.

The structural changes due to heat treatment result in a significant influence on the mechanical properties. Tensile modulus increases on tension heat treatment. On free annealing at 475°C, MePBZT shows lower tensile properties as compared to the as spun fiber. This may partially be a result of skin deep cracks generated as a result of free annealing. However, even with the cracks the torsional modulus and the transverse yield strength of the free annealed MePBZT shows improvement over the tension annealed MePBZT, and over free as well as the tension annealed PBZT fibers. In the torsional modulus calculation, when the diameter is corrected for the crack depth, then for the MePBZT- 475-N-F sample, a torsional modulus value of 4.5 GPa is predicted. Based on this torsional modulus value and the observed linear relationship between the compressive strength and the torsional modulus, a compressive strength value of more than 1 GPa is predicted for the 475-N-F MePBZT fiber. This predicted improvement in compressive strength is attributed to crosslinking in the free annealed sample. A comparison of properties between PBZT (530-N-T1) and MePBZT (530-N-T1) is also meaningful in this regard. Recoil compressive strength, loop strength, torsional modulus, and transverse compressive yield strength - all show that the MePBZT (530-N-T1) fiber has 50 to 100% higher values as compared to the corresponding values for the PBZT (530-N-T1) fiber. It should be noted that the MePBZT (530-N-T1) at best has limited intrafibrillar crosslinking, and no crosslinking in the fiber skin. This suggests that



even with the moderate level of interfibrillar crosslinking, moderate improvement in compressive strength are possible. Significant crosslinking, both inter and intrafibrillar as seen for 475-N-F, can result in dramatic compressive strength improvements, provided the crosslinking can be achieved without creating significant defects in the fiber.

One point that needs further consideration is the observed high recoil compressive strength value of 0.78 GPa for the as spun MePBZT fiber. Even though As MePBZT, in the tensile stress range to which it is subjected during recoil, does not exhibit any hysteresis, the entire tensile stress-strain curve is quite non-linear and exhibits a yield point. The stress-strain behavior of the as spun MePBZT fiber in compression is not known. Due to the possibility of nonlinearity in compression and the energy loss during recoil, we are reluctant to ascribe the above value as the true compressive strength of the fiber. However the compressive strength of this fiber merits further investigation, particularly from the point of view that if 0.78 GPa represents the true compressive strength of the AsMePBZT fiber, then this might suggest a significant influence of the position and presence of the methyl pendant group on compressive strength.

We have confirmed the linear relationship between the recoil compressive strength and the torsional modulus, with few exceptions. One of the exceptions being the high recoil compressive strength of As MePBZT fiber, which has been discussed above. The linear relationship between compressive strength and torsional modulus lends support to the buckling instability as the mechanism for

compression failure. However, we also observe compressive strength and torsional modulus increase with crosslinking, suggesting initiation of compression failure at the molecular level. From these observations, it appears that the buckling initiation occurs at the molecular, rather than the microfibrillar/fibrillar level.

Kink angles and five types of kink geometries have been identified in high performance rigid-rod polymeric fibers. Helical kinks are observed in PPTA and not in PBX fibers. Kinks with a discontinuous line of propagation (i.e. kink propagation across the diameter accompanied with deflection in the longitudinal direction) were commonly observed in the PBX fibers. Compression kink angles in the AsMePBZT and in tension annealed MePBZT are not significantly different from the kink angles in PBZT.

#### 2.6.2 Conclusions:

- (1) It has been demonstrated that the lack of dissolution is the necessary but not the sufficient condition for crosslinking in the rigid rod polymers.
- (2) Crosslinking in the MePBZT fibers occurs in the 450 to 550°C temperature range under free annealing. Up to 36% crosslinking via methyl bridge between backbones has been demonstrated. Surface cracks are developed in the free annealed samples.
- (3) Free annealed MePBZT fibers develop non-fibrillar structure. Crosslinking in the free annealed samples appears to be both inter- and intra-fibrillar.
- (4) In tension annealed MePBZT, no crosslinking and no cracking were observed in the skin, whereas the core may have some intrafibrillar crosslinking.

- (5) Crosslinking in the MePBZT appears to be in the disordered regions.
- (4) Recoil compressive strength, loop strength, torsional modulus and the transverse compressive strength of the tension heat treated MePBZT fiber are 50 to 100% higher as compared to the comparably heat treated PBZT fiber. Axial compressive strength in excess of 1.0 GPa is predicted for MePBZT free annealed at 475°C. This clearly establishes that the crosslinking results in significant compressive strength increase.

## 2.7 SYNTHESIS

Attempts have been made to synthesize new crosslinkable rigid rod polymeric structures. Poly(benzobisthiazole)s containing an ortho-tetrasubstituted biphenyl moiety were synthesized via the polymerization of 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2,2'-dinitro-6,6'-dimethylbiphenyl-4,4'-dicarboxylic acid. Sulfolane was used as a cosolvent with poly(phosphoric acid) (PPA) owing to insolubility of the ortho-tetrasubstituted biphenyl monomer in PPA. The intrinsic viscosities of the polybenzobisthiazoles in methanesulfonic acid at 30°C were in the range of 0.5 to 2.3 dl/g. Copolymerizations of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthalic acid and 2,2'-dinitro-6,6'-dimethylbiphenyl-4,4'-dicarboxylic acid were carried out as well by varying the ratio of the two dicarboxylic acid monomers in the reaction mixture. Intrinsic viscosities of up to 9.93 dl/g were achieved for copolymers. Thermal stability of the copolymers was evaluated by thermogravimetric analysis. Stability of the copolymers was found to

decrease with the increased amount of the substituted biphenyl structure in the polymer backbone. These polymers, if their intrinsic viscosity is greater than 15 dl/g, are desirable candidates as precursor for post-processing owing to the low degradation temperature of pendant groups in the substituted biphenyl structure. (X. Hu, S. Kumar, and M. B. Polk, "Synthesis and Characterization of Poly(benzobisthiazole) with a Substituted Biphenyl Moiety in the Main Chain". Accepted for publication in *Macromolecules*.)

## 2.8 SOLUTION STUDIES:

Lewis acid complexation mediated solubilization of PBZT in nitromethane, can be used for processing dilute polymer solutions into films and coatings. The potential for spinning fibers from anisotropic solutions of PBZT in  $\text{AlCl}_3$ /nitroalkanes is still a fertile area for exploration. Evaluation of properties of fibers spun from polymer complex solutions can provide insight into the role of intermolecular interactions in determining the mechanical properties of such rigid-rod polymers. High molar ratios of  $\text{AlCl}_3$  to PBZT were required to obtain relatively stable solutions of PBZT- $\text{AlCl}_3$  complex. Marginal molar ratios of  $\text{AlCl}_3$ :PBZT 1:4 or just greater either resulted in a gel or the solutions tended to gel even in a controlled inert atmosphere. Extensive dilution of the polymer complex solution with nitroalkane reverses the EDA complexation equilibria toward decomplexation or formation of free PBZT establishing a minimum concentration requirement for  $\text{AlCl}_3$  besides a certain molar excess relative to PBZT. Spectroscopic evidence for the

polymer-Lewis Acid interaction could be obtained in solution by  $^1\text{H}$  as well as  $^{27}\text{Al}$  NMR. The  $^1\text{H}$  spectrum of PBZT in  $\text{AlCl}_3/\text{CD}_3\text{NO}_2$  seems to indicate the presence of more than a single, symmetrically complexed polymer species in solution.  $^{27}\text{Al}$  NMR indicated two different tetra co-ordinate environments for the Al nucleus due to the various donor-acceptor complexation equilibria established between the polymer and the Lewis Acid and also between the Lewis Acid and the solvent. FTIR spectra of the reddish orange solids obtained after evaporation of the solvent from PBZT- $\text{AlCl}_3$  complex solutions of various compositions showed significant intensity variations in the hetero ring absorption bands relative to the IR spectrum of pristine or regenerated PBZT. The red gel from a 1:4 PBZT: $\text{AlCl}_3$  composition in nitromethane could presumably arise from partial complexation between PBZT molecules and  $\text{AlCl}_3$ . Not only are there structural differences indicated in the solid state FTIR of the gel relative to the solids from compositions with a larger molar excess of  $\text{AlCl}_3$  in the initial composition but the gel also shows a unique exothermic behavior in the DSC in contrast to PBZT: $\text{AlCl}_3$  compositions with higher  $\text{AlCl}_3$  content relative to PBZT. A preliminary comparison between the pristine PBZT fibers and regenerated PBZT by dilute solution viscometry seems to indicate that the process of complexation-regeneration using the Lewis acid results in some polymer degradation. More extensive investigations involving different compositions, complexation and regeneration conditions would be needed to fully evaluate this process vis-a-vis the currently established processing route using strong protonic solvents. (N. Venkatasubramanian, M.B. Polk, Satish Kumar, and L.

T. Gelbaum, "Structural Investigations on Lewis Acid-Mediated Solubilization of poly (p-phenylenebenzobisthiazole) in an Aprotic Solvent". J. Polym. Sci. (Phys ed.), 31 (1993) p. 1965-1973.)